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Ferroelectric and magnetic properties of Pb(Fe2/3W1/3)O3-based multiferroic compounds with cation order

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Abstract
BiFeO3 and PbTiO3 were introduced to a Sc-modified Pb(Fe2/3W1/3)O3 compound with strong cation order to improve the multiferroic properties. It is found that the degree of cation order decreases as the amount of BiFeO3 or PbTiO3 increases. As a result, the saturation magnetization deteriorates. Solid solutions with BiFeO3 show an increase in both ferroelectric and magnetic transition temperatures. However, the ferroelectric remanent polarization is dramatically suppressed. In contrast, solid solution with PbTiO3 leads to an increase in the ferroelectric transition temperature, a decrease in the magnetic transition temperature, and a significant enhancement of remanent polarization. The composition 0.93[0.79Pb(Fe2/3W1/3)O3–0.21Pb(Sc2/3W1/3)O3]–0.07PbTiO3 shows the optimized properties of Tmax of 208K, Pr of 3.6μC/cm2 between 120 and 210K, TN of 209K, and Ms of 0.23μB/f.u. (3.7emu/g) at 10K under 5T.

Keywords
Ames Laboratory, Ozone, Lead, Ceramics, Solid solutions, Polarization, Ferroelectric phase transitions, Saturation moments, Curie point, Dielectric oxides, Multiferroics

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Ferroelectric and magnetic properties of $Pb(Fe_{2/3}W_{1/3})O_3$-based multiferroic compounds with cation order

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$BiFeO_3$ and $PbTiO_3$ were introduced to a Sc-modified $Pb(Fe_{2/3}W_{1/3})O_3$ compound with strong cation order to improve the multiferroic properties. It is found that the degree of cation order decreases as the amount of $BiFeO_3$ or $PbTiO_3$ increases. As a result, the saturation magnetization deteriorates. Solid solutions with $BiFeO_3$ show an increase in both ferroelectric and magnetic transition temperatures. However, the ferroelectric remanent polarization is dramatically suppressed. In contrast, solid solution with $PbTiO_3$ leads to an increase in the ferroelectric transition temperature, a decrease in the magnetic transition temperature, and a significant enhancement of remanent polarization. The composition $0.93[0.79Pb(Fe_{2/3}W_{1/3})O_3-0.21Pb(Sc_{2/3}W_{1/3})O_3]-0.07PbTiO_3$ shows the optimized properties of T_{max} of 208 K, P_r of 3.6 $\mu C/cm^2$ between 120 and 210 K, T_N of 209 K, and M_s of $0.23\mu_B$/f.u. (3.7 emu/g) at 10 K under 5 T. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2818367]

I. INTRODUCTION

Magnetoelectric multiferroic compounds, combining a spontaneous electrical polarization with a net magnetization, have attracted worldwide interest recently due to their great potentials for fundamental research and practical applications.[1–3] However, all the known magnetic ferroelectric oxides either have a low transition temperature or display an extremely small polarization/magnetization. Among these multiferroic compounds, those with the ABO_3 perovskite structure show the highest magnetic transition temperatures and the largest electrical polarizations.[3] Considering the fact that most magnetic perovskite oxides have an antiferromagnetic order due to a superexchange coupling between magnetic ions on the *B* site,[4] large saturation magnetization can be realized via *ferrimagnetism* through cation ordering.[5,6]

The multiferroic $Pb(Fe_{2/3}W_{1/3})O_3$ compound shows 1:1 cation order; however, the chemical order is very weak and the cation ordered domains are limited to the nanometer scale (<5 nm).[7–9] Recently, we have demonstrated experimentally that substituting the Fe^{3+} in $Pb(Fe_{2/3}W_{1/3})O_3$ with Sc^{3+} can lead to long range cation order and consequently to large saturation magnetization (up to $0.61\mu_B$/f.u.).[10] At the same time, well-defined saturated polarization versus electric field hysteresis loops were recorded at 120 K under quasistatic (4 Hz) strong (40 kV/cm) electric fields.[10] However, the ferroelectric properties of these ceramics need to be further improved at higher temperatures. In the present work, the ceramic $0.79Pb(Fe_{2/3}W_{1/3})O_3-0.21Pb(Sc_{2/3}W_{1/3})O_3$ (abbreviated as PFSW21 hereafter) is used as the base compound due to its strong cation order (ordering parameter of 0.8). $BiFeO_3$ (BF) and $PbTiO_3$ (PT) were employed to form solid solutions with PFSW21 to improve the ferroelectric properties. $BiFeO_3$ is selected because of its multiferroism,[11,12] high ferroelectric and magnetic transition temperatures,[11–15] and large ferroelectric remanent polarization.[11,15] $PbTiO_3$ is used because of its high ferroelectric transition temperature, large polarization, and strong ability to stabilize the perovskite phase.[16]

II. EXPERIMENTAL PROCEDURE

Ceramics in the solid solutions $(1-x)$PFSW21-xBF ($x=0.00, 0.04, 0.10$) and $(1-x)$PFSW21-xPT ($x=0.00, 0.07, 0.10$) were prepared via a solid state reaction method with high purity powders (better than 99.9%). Proportional amount of *B*-site cation oxides Fe_2O_3, WO_3, Sc_2O_3 (and TiO_2 for PT solid solutions) powders were mixed and calcined at 900 °C for 24 h. Then an appropriate amount of PbO (and Bi_2O_3 for BF solid solutions) powder was mixed and a second calcination was carried out at 850 °C for 2 h. Ceramic pellets of $(1-x)$PFSW21-xBF were formed by sintering at 910 °C for 1 h followed by a slow cooling procedure at 9 °C/h to 850 °C. Pellets of $(1-x)$PFSW21-xPT were sintered at 1000–1050 °C for 0.5 h followed by a slow cooling procedure at 9 °C/h from 900 to 800 °C.

The surface layers of the sintered disks were removed by mechanical grinding and x-ray diffraction was used to verify the phase purity. Dielectric characterization was performed with an *LCR* meter (HP-4284A, Hewlett-Packard) in conjunction with an environmental chamber (9023, Delta Design). A heating rate of 3 °C/min was used during measurement. The polarization hysteresis measurement was carried out with a standardized ferroelectric test system (RT-66A,

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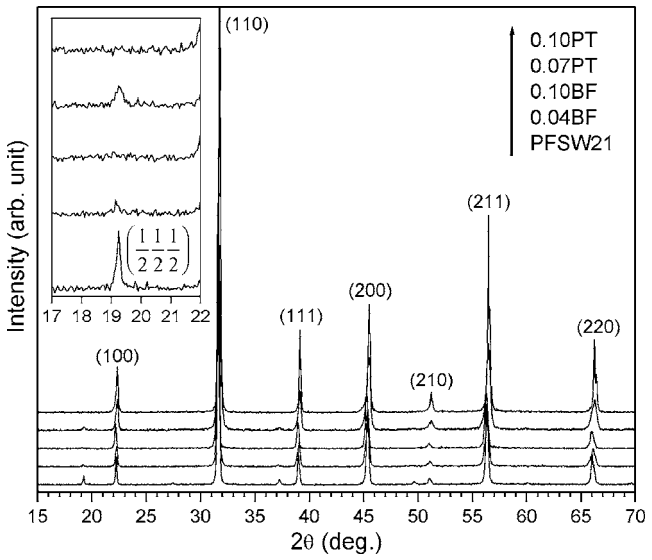

FIG. 1. X-ray diffraction patterns of the $(1-x)$PFSW21-xBF and the $(1-x)$PFSW21-xPT ceramics. Major peaks are indexed on the basis of a simple cubic perovskite structure. The $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ superlattice peak due to B-site cation order is replotted in the inset for clarity.

Radiant Technologies). A Quantum Design 5 T magnetic properties measurement system was used for magnetic characterization.

III. RESULTS

A. Phase purity and structure analysis

X-ray diffraction indicates that the as-sintered ceramics are phase pure and display a pseudocubic perovskite structure, as shown in Fig. 1. The lattice parameters determined from the x-ray diffraction results of these ceramics are listed in Table I. It is evident that the lattice parameter decreases as the amount of $PbTiO_3$ increases in the $(1-x)$PFSW21-xPT solid solution. This is consistent with the fact that Ti^{4+} has a smaller radius on the B site. However, there is no clear trend for the lattice parameter in the $(1-x)$PFSW21-xBF solid solution where A-site substitution also takes place.

As shown previously, a strong $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ superlattice peak was observed in the PFSW21 ceramic.[10] Close examination in this range for other ceramics, as revealed by the inset in Fig. 1, indicates that incorporating $BiFeO_3$ or $PbTiO_3$ into PFSW21 gradually diminishes the super lattice peak. In complex perovskite oxides, the presence of the $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ superlattice peak is an indication of the development of 1:1 B-site cation order and the intensity of this superlattice peak has been routinely used to calculate the ordering parameter S.[17,18] This parameter ranges from 0 to 1, with 0 marking the complete disorder and 1 marking the complete order. The ordering parameter S is calculated for these ceramics and is also listed in Table I. It is noted that a fairly high degree of B-site cation order is still preserved in the ceramics of 0.96PFSW21-0.04BF and 0.93PFSW21-0.07PT.

TABLE I. The lattice parameter a and the cation ordering parameter S of the ceramics.

	a (Å)	S
PFSW21	4.0004	0.8
0.96PFSW21–0.04BF	3.9895	0.5
0.90PFSW21–0.10BF	4.0011	0.2
0.93PFSW21–0.07PT	3.9885	0.6
0.90PFSW21–0.10PT	3.9814	0.0

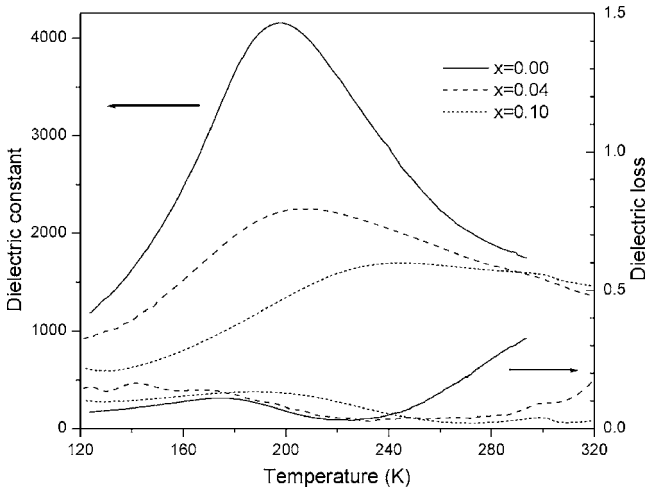

FIG. 2. Relative dielectric permittivity and dielectric loss of the $(1-x)$PFSW21-xBF ceramics as a function of temperature at 100 kHz.

B. Ferroelectric and magnetic properties of $(1-x)$PFSW21-xBF

The dielectric response of the 0.96PFSW21-0.04BF and 0.90PFSW21-0.10BF ceramics was examined at 100 kHz and the results are shown in Fig. 2. For comparison, the dielectric properties of PFSW21 are also included. It is noted that solid solution with $BiFeO_3$ shifts the dielectric peak to higher temperatures and effectively suppresses the dielectric loss at temperatures above 240 K. Unfortunately, incorporating $BiFeO_3$ at the same time leads to a significant reduction in the peak dielectric constant ε_{max} and a further broadening of the dielectric peak at T_{max}.

The low dielectric loss at low temperatures allows the electric-field-induced polarization measurement under strong quasistatic fields. The electrical polarization versus electric field hysteresis loop was evaluated at 4 Hz under the peak fields of 40 kV/cm at a series of temperatures up to 190 K for 0.96PFSW21-0.04BF and 230 K for 0.90PFSW21-0.10BF, respectively. As shown in Fig. 3, the loops are not saturated and open up as temperature increases, which may be attributed to the leakage current. Compared to PFSW21, it is apparent that 0.96PFSW21-0.04BF and 0.90PFSW21-0.10BF can sustain strong quasistatic electric fields at much higher temperatures. However, the remanent polarization P_r is significantly reduced in both ceramics.

The magnetization under weak field as a function of temperature for the ceramics is given in Fig. 4(a). There is a clear transition from paramagnetic to ferrimagnetic at ~222 K for the PFSW21 ceramic. Maxima of spontaneous magnetization of $0.12\mu_B$, $0.014\mu_B$, and $0.003\mu_B$ per ABO_3 f.u. were measured under 100 Oe for $x=0.00$, 0.04, and 0.10 in the $(1-x)$PFSW21-xBF solid solution system. The magnetization under a stronger magnetic field of 10 kOe for the

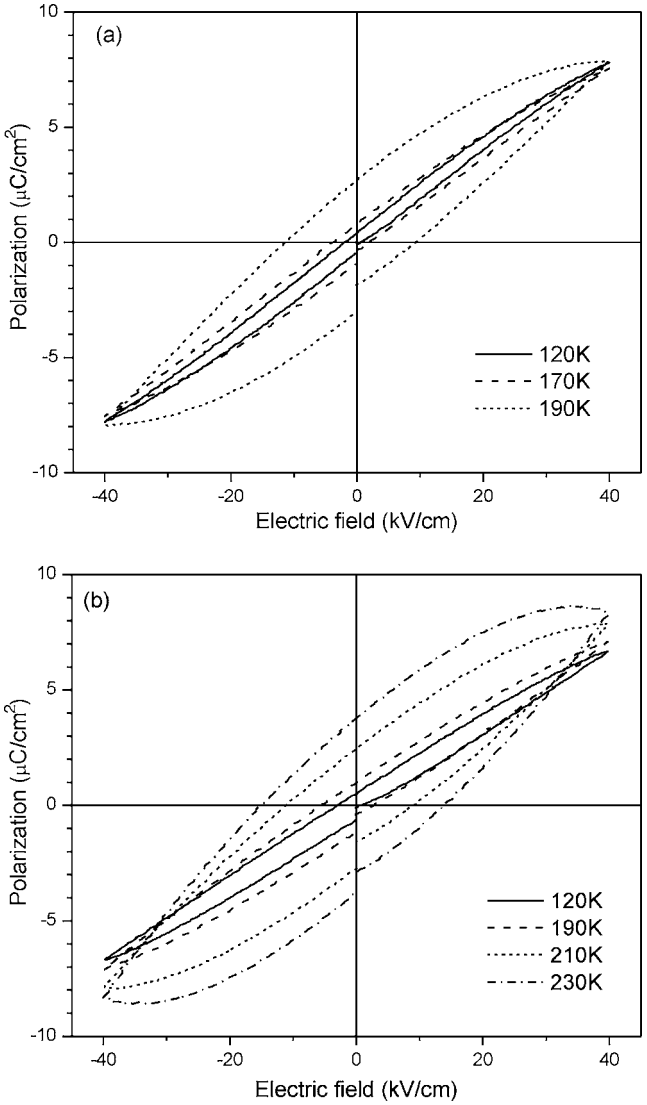

FIG. 3. Polarization vs electric field hysteresis loops measured at 4 Hz at a series of temperatures in (a) the 0.96PFSW21-0.04BF ceramic and (b) the 0.90PFSW21-0.10BF ceramic.

three ceramics is shown in Fig. 4(b). The saturation magnetizations at 10 K under 10 kOe were determined to be $0.38\mu_B$/f.u., $0.11\mu_B$/f.u., and $0.05\mu_B$/f.u. for $x=0.00$, 0.04, and 0.10 in the $(1-x)$PFSW21-xBF solid solution system. Therefore, incorporating $BiFeO_3$ deteriorates the saturation magnetization due to the disruption of the cation order.

C. Ferroelectric and magnetic properties of $(1-x)$PFSW21-xPT

The dielectric response of the 0.93PFSW21-0.07PT and 0.90PFSW21-0.10PT ceramics, together with PFSW21, is shown in Fig. 5. Similar to the results shown in Fig. 2, solid solution with $PbTiO_3$ also shifts the dielectric peak to higher temperatures and effectively suppresses the dielectric loss in the whole measurement temperature range. However, in sharp contrast to the case of $(1-x)$PFSW21-xBF, solid solution $(1-x)$PFSW21-xPT displays a significant increase in the peak dielectric constant ε_{max} and a sharpening of the dielectric peak at T_{max}.

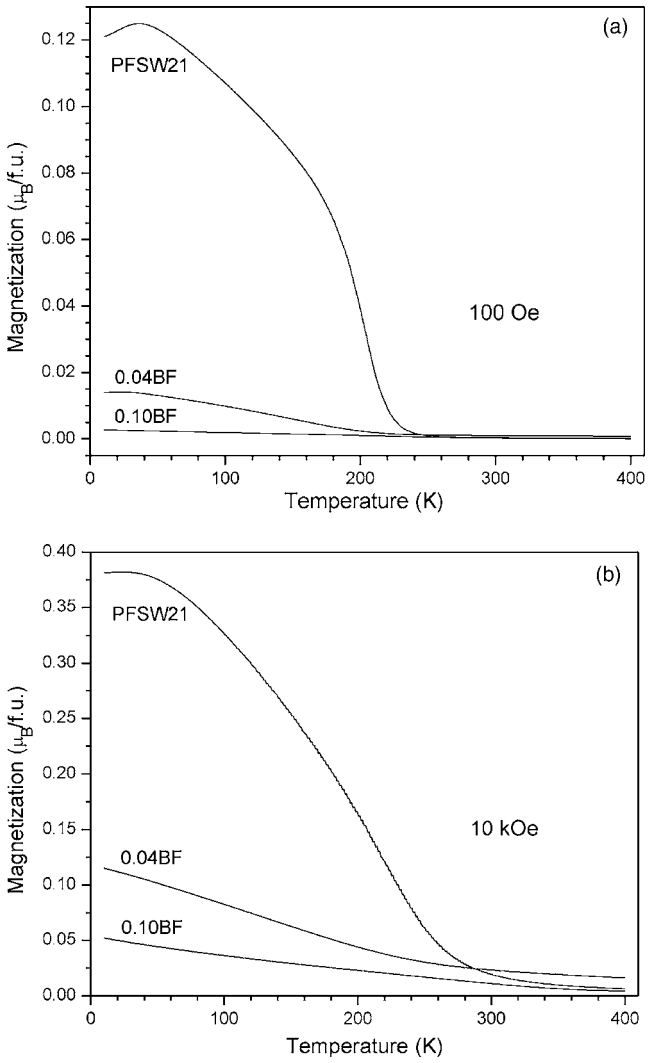

FIG. 4. Magnetization vs temperature during cooling under (a) 100 Oe and (b) 10 kOe in the $(1-x)$PFSW21-xBF ceramics.

The electrical polarization versus electric field hysteresis loop was evaluated at 4 Hz at a series of temperatures and is shown in Fig. 6. Well-defined and saturated hysteresis loops under the peak fields of 40 kV/cm can be recorded up to

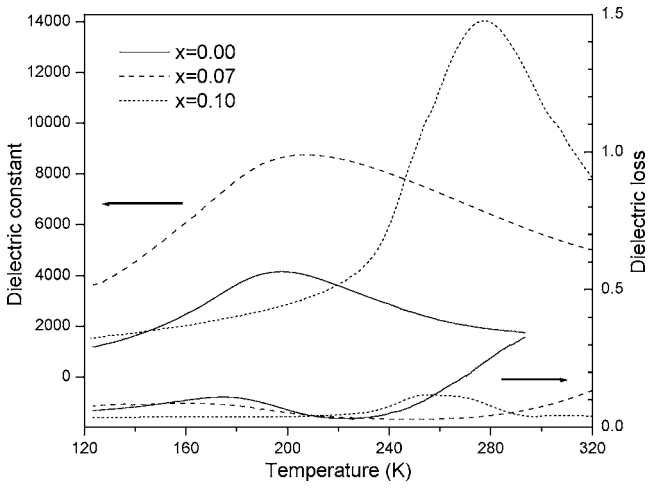

FIG. 5. Relative dielectric permittivity and dielectric loss of the $(1-x)$PFSW21-xPT ceramics as a function of temperature at 100 kHz.

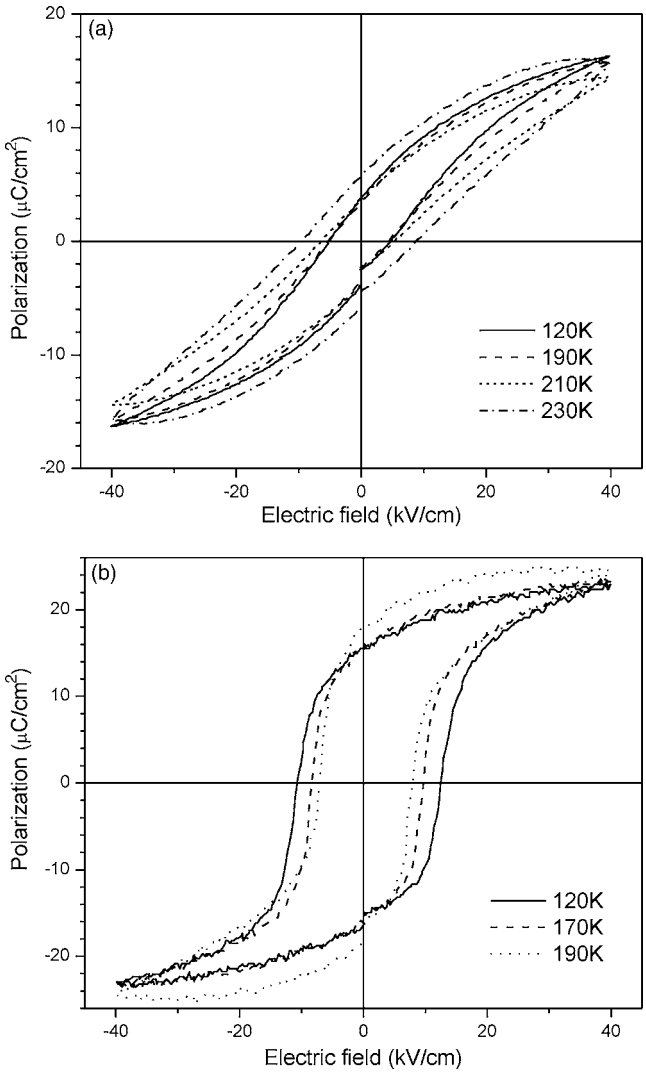

FIG. 6. Polarization vs electric field hysteresis loops measured at 4 Hz at a series of temperatures in (a) the 0.93PFSW21-0.07PT ceramic and (b) the 0.90PFSW21-0.10PT ceramic.

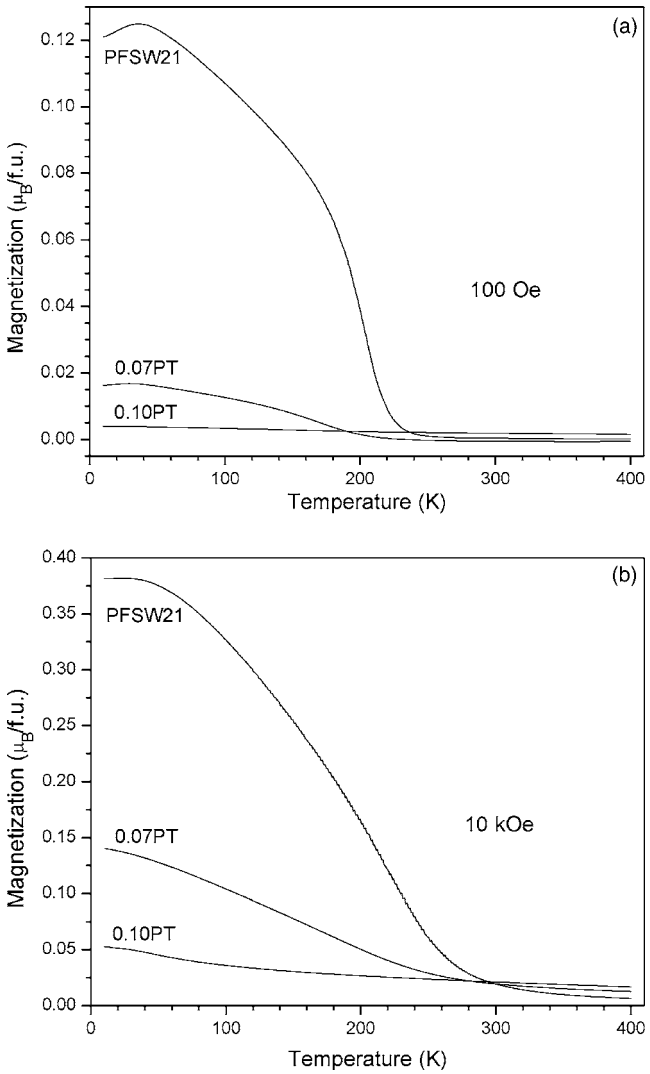

FIG. 7. Magnetization vs temperature during cooling under (a) 100 Oe and (b) 10 kOe in the $(1-x)$PFSW21-xPT ceramics.

230 K for 0.93PFSW21-0.07PT and 190 K for 0.90PFSW21-0.10PT. Compared to PFSW21, the 0.93PFSW21-0.07PT ceramic maintains a similar remanent polarization P_r to much higher temperatures while the 0.90PFSW21-0.10PT ceramic displays a fourfold increase in P_r.

The magnetization under weak field as a function of temperature for the ceramics is given in Fig. 7(a). Maxima of spontaneous magnetization of $0.12\mu_B$/f.u., $0.017\mu_B$/f.u., and $0.004\mu_B$/f.u. were measured under 100 Oe for $x=0.00$, 0.07, and 0.10 in the $(1-x)$PFSW21-xPT solid solution system. The magnetizations under a stronger magnetic field of 10 kOe for the three ceramics are shown in Fig. 7(b). The saturation magnetizations at 10 K under 10 kOe were determined to be $0.38\mu_B$/f.u., $0.14\mu_B$/f.u. and $0.05\mu_B$/f.u. for $x=0.00$, 0.07, and 0.10 in the $(1-x)$PFSW21-xPT solid solution system. Similar to $BiFeO_3$, incorporating $PbTiO_3$ also deteriorates the magnetization of the ceramics.

The 0.93PFSW21-0.07PT ceramic appears to have the highest saturation magnetization at 10 K under 10 kOe, compared to 0.96PFSW21-0.04BF, 0.90PFSW21-0.10BF, and 0.90PFSW21-0.10PT. So, this ceramic was subjected to further magnetic measurements. The magnetization under a magnetic field of 50 kOe is shown in Fig. 8, where the data for PFSW21 are also plotted for comparison. The saturation magnetization at 10 K was determined to be $0.23\mu_B$/f.u., about half of that of PFSW21 under the same condition. The magnetic hysteresis loop of the 0.93PFSW21-0.07PT ceramic measured at 10 K is shown in Fig. 9. The inset of Fig. 9 shows the central portion of the hysteresis loop. The remanent magnetization of the ceramic was measured to be is $0.024\mu_B$/f.u. and the coercive field is 190 Oe.

IV. DISCUSSION

In the development of single phase magnetoelectric multiferroic compounds, compromises have to be made in balancing the ferroelectric and magnetic properties.[14] Among the properties of primary importance are the ferroelectric transition temperature, the remanent polarization, the magnetic transition temperature, and the saturation magnetization. These properties measured in the present work are summarized in Table II.

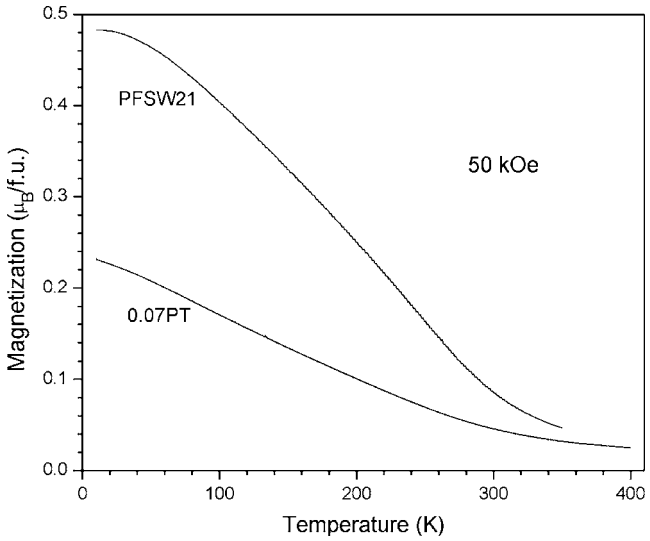

FIG. 8. Magnetization vs temperature during cooling under 50 kOe in the PFSW21 and the 0.93PFSW21-0.07PT ceramics.

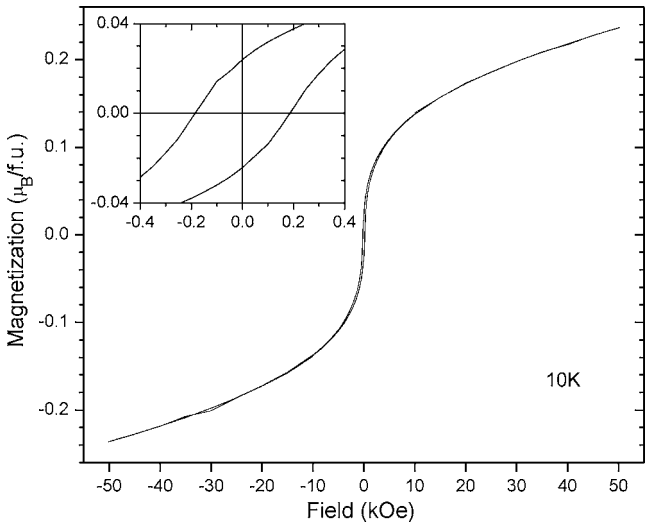

FIG. 9. Magnetization vs magnetic field hysteresis loop measured at 10 K in the 0.93PFSW21-0.07PT ceramic. The inset reveals the coercive field and the remanent magnetization.

The base compound, PFSW21, has a superior saturation magnetization due to the presence of a strong cation order.[10] The remanent polarization (3.8 $\mu C/cm^2$) is comparable to that of bulk $BaTiO_3$ ceramics and the ferroelectric transition temperature (198 K) is relatively low. Forming solid solutions with $BiFeO_3$ or $PbTiO_3$ can effectively shift the ferroelectric transition to higher temperatures. However, opposite impacts on the remanent polarization were observed. Incorporating $BiFeO_3$ into PFSW21 diminishes the remanent polarization while incorporating $PbTiO_3$ enhances it. Therefore, when the ferroelectric properties are primarily concerned, $PbTiO_3$ appears to be a better choice to modify PFSW21.

For the magnetic transition temperature, the $(1-x)$PFSW21-xBF solid solution does not show a clear trend. It first decreased in 0.96PFSW21-0.04BF and then increased in 0.90PFSW21-0.10BF. In comparison, a consistent decrease in magnetic transition temperature was observed in the $(1-x)$PFSW21-xPT solid solution system as $PbTiO_3$ content increased. Close examination of the ferroelectric and magnetic transition temperatures in Table II seems to suggest that they can be adjusted independently. A significant implication for this observation is that the solid solution approach may lead to unique compositions in both solid solution systems where the ferroelectric transition temperature coincides with the magnetic transition temperature. For example, the 0.93PFSW21-0.07PT ceramic is close to such unique compositions. For these compositions, a strong magnetoelectric coupling may be expected since both transitions occur at the same temperature.

The saturation magnetization is significantly reduced when $BiFeO_3$ or $PbTiO_3$ is incorporated into PFSW21. In this respect, $BiFeO_3$ and $PbTiO_3$ are similarly detrimental. When the cation ordering parameter S listed in Table I is taken into consideration, it is easy to conclude that there is a direct correlation between the cation order and the saturation magnetization. This again confirms that the degree of B-site cation order dictates the measured magnetization in these complex perovskite oxides.[10]

Comparing the overall effect of $BiFeO_3$ and $PbTiO_3$ on the multiferroic properties of PFSW21, it appears that $PbTiO_3$ is superior to $BiFeO_3$ since it shifts the ferroelectric transition to higher temperatures, preserves the high remanent polarization to higher temperatures, and leads to a slight suppression of the magnetic properties. The magnetic properties, however, can be improved if a base compound other than PFSW21 is used. In PFSW21, the base compound used in the present work, nonmagnetic Sc^{3+} replaces the magnetic Fe^{3+} for the purpose of developing long range B-site cation order. Future work should be focused on the search for a

TABLE II. Summary of ferroelectric and magnetic properties of the ceramics.

	T_{max} (K) at 100 kHz	P_r ($\mu C/cm^2$) at 120 K	P_r ($\mu C/cm^2$) at 190 K	T_N (K)	M_s (μ_B/f.u.) at 100 Oe	M_s (μ_B/f.u.) at 10 kOe, 10 K	M_s (μ_B/f.u.) at 50 kOe, 10 K
PFSW21	198	3.8	/	222	0.12	0.38	0.48
0.96PFSW21–0.04BF	208	0.4	2.5	210	0.014	0.11	/
0.90PFSW21–0.10BF	245	0.4	0.9	312	0.003	0.05	/
0.93PFSW21–0.07PT	208	3.6	3.6	209	0.017	0.14	0.23
0.90PFSW21–0.10PT	277	15.5	17.7	206	0.004	0.05	/

chemical modifier better than Sc^{3+} in terms of developing long range *B*-site cation order and realizing strong magnetism in $Pb(Fe_{2/3}W_{1/3})O_3$. Then, the formation of solid solutions with $PbTiO_3$ should be pursued.

V. CONCLUSIONS

Comparison between the $(1-x)$PFSW21-xBF and $(1-x)$PFSW21-xPT solid solution systems indicates that $PbTiO_3$ is a better choice for improving the multiferroic properties of the cation ordered compound PFSW21. The importance of the cation order for the magnetic properties in these complex perovskite oxides is confirmed. Solid solutions of cation ordered $Pb(Fe_{2/3}W_{1/3})O_3$-based compounds with $PbTiO_3$ are promising for high ferroelectric/magnetic transition temperatures, large remanent polarizations, and high saturation magnetizations.

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